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Modulated DSC studies of $Pb_{1-X}Ca_XTiO_3$ ferroelectric ceramics

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Abstract The polycrystalline ceramic samples of general formula $Pb_{1-X}Ca_XTiO_3$ with $X = 0.00$, 0.1, 0.2 and 0.3 have been synthesized by standard high temperature solid state reaction method using high purity oxide and carbonates. The formation of the single phase compounds have been checked by X-ray diffraction technique. The Modulated Differential Scanning Calorimetry has been used to investigate the effect of substitution on the phase transition temperature and the corresponding change on the enthalpy and other thermal parameters of the substituted compound/solid solutions. It was observed that the phase transition temperature (T_c) decreases linearly with the increase of substitution concentration. The linear decrease in T_c with increase of substitution concentration may be useful for the eventual functionality of the materials for different ferroelectric devices. The results are discussed in detail.

Keywords Curie temperature · Ferroelectrics · Modulated DSC · Oxide ceramics · Phase transition · X-ray diffraction

Introduction

Progress in materials development and characterization has led to the generation and identification of several novel, electronic, optoelectronic and smart materials. Ferroelectric oxide based ceramic materials are most promising for different electronic devices due to their high dielectric, piezoelectric, pyroelectric and electro-optic constants as well as the existence of hysteresis loop with bistable memory states [1–6]. In ABO_3 type perovskite ferroelectrics, A-cation occupies the corners and B-cation occupies the center position in the unit cell with oxygen ions at the centre of the faces. In this type of structure A and B-cation sites may be substituted either fully or partially by the other homovalent or heterovalent cations. It is possible to substitute more than one type of metal ions in the B-cation site for valence compensation [7, 8]. It is also observed that a combination of trivalent and pentavalent cation substitution on the B-site was favorable for the formation of the perovskite structure [9]. However, the large variations of composition are accompanied by changes in structure, which may have profound effect on the other physical properties of the materials. $PbTiO_3$ is one such perovskite type ferroelectric material having the following characteristics: transition temperature $Tc = 763$ K, tetragonality $c/a = 1.064$ and dielectric constant $K = 200$ at room temperature [10]. It has a large crystal anisotropy in the spontaneous polarization and because of this it is very difficult to prepare dense ceramics of pure $PbTiO_3$ [11, 12]. The combinations of divalent and pentavalent materials not only densify the material but also enhance the other physical characteristics. One such divalent additive is Ca, which takes the A-cation site in the perovskite structure. In the literature a large number of works have been reported on pure and substituted compounds/solid solutions in thin films, ceramics and nanoparticle form [13–19]. But no paper reports systematically on the effect of Ca-substitution on the phase transition studies. The present paper reports on the phase transition of $Pb_{1-X}Ca_XTiO_3$ ($X = 0.00$, 0.1, 0.2 and 0.3) using Modulated Differential Scanning Calorimetry (MDSC) studies. The advantage of MDSC over plain DSC is that in MDSC an additional sinusoidal thermal excitation is superimposed as if two

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experiments are running simultaneously. The linear heating rate provides the information about heat flow (enthalpy exchange), whereas the sinusoidal heating rate provides the heat capacity of the material under investigation. Therefore, MDSC gives more quantitative and accurate measurement of heat capacity as well as enthalpy change at the transition temperature. Not only this but complex transitions can also be analyzed more accurately and easily through MDSC, having reversing and relaxing components or events too close to resolve via plain DSC.

Experimental

The polycrystalline ceramic samples of $Pb_{1-X}Ca_XTiO_3$ with $X = 0.00$, 0.1, 0.2 and 0.3 have been prepared using the high purity chemicals PbO, $CaCO_3$ and TiO_2 (99.9% pure obtained from Aldrich chemicals Co USA and CDH Bombay) by standard solid state reaction technique. The stoichiometric amounts of these oxides and carbonates were mixed and milled for several hours and then calcined at 1,073–1,173 K for 24 h. The process of milling and calcinations was repeated for a number of times and finally cylindrical pellets were made after applying pressure around 498 MPa (5 tones/cm^2) in a hydraulic press. These pellets were sintered at $\sim$1,423 K for 4–6 h. The formation of the single phase solid solutions was confirmed by X-ray diffraction technique using the Rigaku X-ray diffractometer with CuK_α radiation and nickel filter in a wide range of 2θ from 10–90^o with a scanning rate of 2^o/min. The instrument was calibrated using the pure silicon sample provided with the instrument. The surface morphology as well as particle/grain size was measured by scanning electron microscopy (SEM) using the JEOL, JSM-5600 SEM with different magnifications in back scattered mode. The modulated DSC measurement was carried out on TA Instruments Model 2910 MDSC equipment from room temperature (RT) to 873 K in inert (N_2) atmosphere with a heating rate of 5 K/min and ±0.75 K modulation per 60 s.

Results and discussion

It has been observed that the X-ray powder diagrams of $Pb_{1-X}Ca_XTiO_3$ with $X = 0.1$, 0.2 and 0.3 are quite similar with that of the pure ($X = 0.00$) compound. Comparisons between observed and calculated interplanar spacings (d-values) are in good agreement with each other. To get a clear insight into the Ca-substitution effect on the lattice, it is observed that the tetragonality ratio *c/a* is almost constant. The expansion and contraction of the lattice parameters along *a*- and *c*-axes with the substitution of Ca^{2+} ion in place of Pb^{2+} ion are so small that the lattice distortion is least and *c/a* ratio remains invariant. Thus X-ray analysis of all the samples indicates that the specimens are of single phase perovskite type tetragonal structure with space group P4 mm.

The comparison of the morphology obtained from the SEM micrograph of the pure and substituted solid solutions revealed that the particles of the pure compound are larger than the average particle size of the substituted solid solutions. The distribution of particles in the pure compound is not very regular nor compact and shows voids in between the grains even after applying proper sintering conditions of time and temperature as shown in Fig. 1a. Due to this pure compound is often brittle and shows very high value of T_c. The average particle size of the pure compound is around 5 μm. With the gradual increase of substitution concentration of Ca^{2+} in place of Pb^{2+} on A-cation site, the binding strength among the particles/grains increases causing the reduction in particle size and hence enhanced density. A typical comparison of the SEM micrographs for $X = 0.00$ and $X = 0.2$ are shown in Fig. 1a, b.

Figure 2(a, b, c, d) shows DSC curves of $Pb_{1-X}Ca_XTiO_3$ with $X = 0.00$, 0.1, 0.2 and 0.3. From the figure it is evident that the pure compound undergoes an endothermic peak superimpose on it an exothermic peak indicating ferroelectric phase transition at 761 ± 2 K. The sharpness of endothermic and exothermic peak at transition temperature (T_c) indicates that the quality of the compound is highly pure. Apart from this no other transition has been observed in the measured temperature region which is consistent with the earlier report [6]. Due to modulated heating profile which is superimposed on the normal

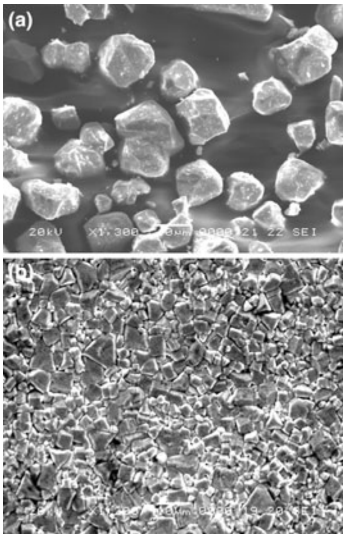

Fig. 1 SEM micrographs of $Pb_{1-X}Ca_XTiO_3$ for $X = 0.0$ and $X = 0.2$

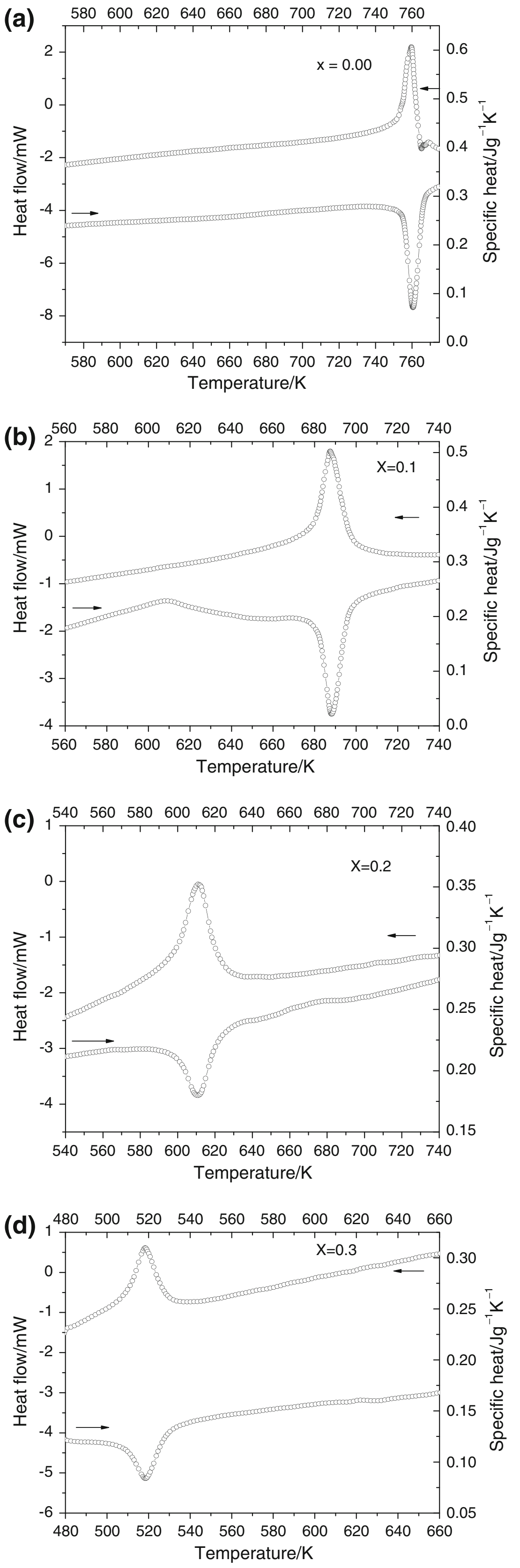

Fig. 2 Specific heat/Heat flow vs. Temperature curve of $Pb_{1-X}Ca_XTiO_3$ for $X = 0.0$, 0.1, 0.2 and 0.3

heating profile, we observed an exothermic peak just above the endothermic peak at T_c. Not only this, the modulated DSC curves give the direct measurement of specific heat (*Cp*) of the material at T_c. The symmetrical and sharp peak with no other peak in the measured temperature region indicates better thermal stability without impurity phase of the material.

When Ca^{2+} ion is substituted in small concentration ($X = 0.1$) in place of Pb^{2+} ion on the A-cation lattice site, the T_c peak is shifted towards lower temperature value of $\sim$687 K without any change in other material characteristics except the amplitude of the modulated profile (exothermic peak) is higher than the normal profile (endothermic peak). When the substitution concentration increases from $X = 0.1$ to $X = 0.2$, the T_c decreases from $\sim$687 to $\sim$611 K (Fig. 2c). In this case also the amplitude of the exothermic peak is larger then the endothermic peak but the sharpness of the peak decreases which may be due to small distortion in A-cation lattice site with the increase of Ca^{2+} concentration. Further increase of concentration from $X = 0.2$ to $X = 0.3$, the T_c shifted from 611 to 518 K with a slight reduction in the amplitude of the endothermic peak and increase in the amplitude of exothermic peak. The broadness of the endothermic peak is more than the exothermic peak which indicates that the lattice distortion is slight more with the increase of Ca^{2+} ion concentration on the A-cation site due to difference in ionic size of the two cation Pb^{2+} (1.35Å) and Ca^{2+} (1.20Å) and its different thermal characteristics [16]. Table 1 shows a systematic change in T_c, *Cp* and *ΔH* (enthalpy change) with the increase of Ca^{2+} ion concentration on the A-cation lattice site. It is interesting to note that the reduction in *Cp* value for $X = 0.2$ is more than that of $X = 0.3$ which needs further explanation. The plot of T_c and the substitution concentration shows an inverse relationship as substitution concentration increases, the phase transition temperature T_c decreases.

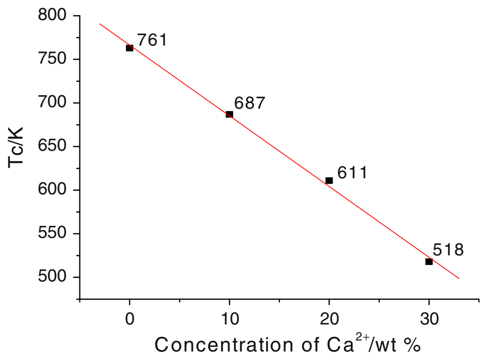

Fig. 3 Variation of T_c with the concentration of Ca^{2+} ion in $Pb_{1-X}Ca_XTiO_3$. ($X = 0.00$, 0.1, 0.2 and 0.3)

Table 1 Variation of T_c with concentration of Ca^{2+} ion in $Pb_{1-x}Ca_xTiO_3$ and its corresponding Cp and ΔH values

Substitution concentration in $Pb_{1-x}Ca_xTiO_3$	Transition temperature (T_c) K	Specific heat (Cp) Jg^{-1} K^{-1}	Enthalpy change (ΔH) Jg^{-1}
$X = 0.00$	761 ± 2	0.61	2.42
$X = 0.1$	687	0.51	2.38
$X = 0.2$	611	0.35	1.58
$X = 0.3$	518	0.31	1.44

Conclusions

From the above studies it is concluded that the pure $PbTiO_3$ compound shows very high value of T_c of $\sim$763 K and very brittle due to its poor binding strength and hence creating practical difficulty in device application. But with the gradual increase of the homovalent isoelectronic cation substitution on A-cation site, the binding strength increases which is also responsible for the increase in the thermal stability and decrease in T_c as well as reduction in particle size (enhanced density) of the substituted compounds. Thus we see that with the substitution of isoelectronic foreign atom on the A-cation site of the host lattice, the material characteristics get improved and provide better results for eventual functionality.

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